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(54) Title of the Invention: Treatment Methods and Apparatuses of Chlorine Substance

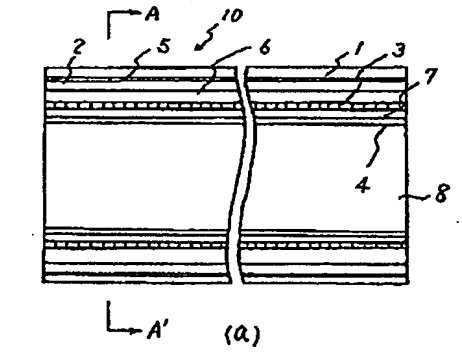
(57)[Abstract Of the Invention]

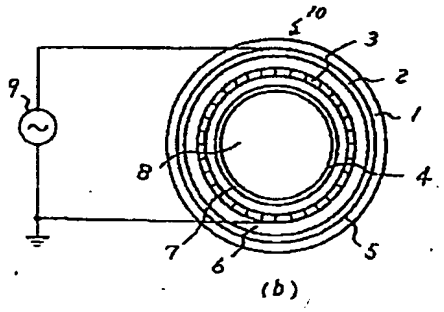
[Subject]

Hitherto, the mercury-vapor lamp is used as ultraviolet ray generator, and accordingly there is a drawback that its decomposition capability for chlorofluorocarbon is low because of its insufficient intensity of rays.

[Means for Solving the Subject]

A flow of chlorofluorocarbon is made through a decomposition process area 8 which is an inner area of cylindrical window tube 4 through which vacuum ultraviolet rays pass. A high voltage cylindrical electrode 1 of which the surface has a mirror finish, an insulating tube 2, and a meshed cylindrical electrode 3 are arranged in a coaxially cylindrical shape. In a discharge space 6 between the meshed cylindrical electrode 3 and the insulating tube 2, a gas, such as xenon which shall emit rays of 120 to 180 (nm) wavelength, is encapsulated. By applying a





polarity alternating voltage between the high voltage cylindrical electrode 1 and the meshed cylindrical electrode 3, dielectric barrier discharge occurs in the discharge space 6. Vacuum ultraviolet rays generated in the process of dielectric barrier discharge pass through the meshed cylindrical electrode 3 and then pass through the cylindrical window tube 4 positioned in an arbitrary distance from the meshed cylindrical electrode 3. With the rays, chlorofluorocarbon flowing through the cylindrical window tube 4 is irradiated and the chlorofluorocarbon is photodecomposed and disposed of as chlorine gases and/or chlorine-based polymers.

[Scope of Claims]

[Claim 1]

A treatment method of chlorine substance characterized by irradiating chlorine substance in an oxygen mixed atmosphere with vacuum ultraviolet rays of 120 to 180 (nm) wavelength and thus decomposing chlorine substance.

[Claim 2]

A treatment method of chlorine substance characterized by irradiating chlorine substance in an oxygen mixed atmosphere with fluorescent light from xenon excimer and thus decomposing chlorine substance.

[Claim 3]

An apparatus for decomposing chlorine substance comprising: a container for intake of chlorine substance; maintaining oxygen atmosphere means for maintaining an oxygen mixed atmosphere in the container; and irradiation means for irradiating chlorine substance intake into the container with vacuum ultraviolet rays of 120 to 180 (nm) wavelength.

[Claim 4]

An apparatus for decomposing chlorine substance comprising: a

container for intake of chlorine substance; maintaining oxygen atmosphere means for maintaining an oxygen mixed atmosphere in the container; and irradiation means for irradiating chlorine substance intake into the container with fluorescent light from xenon excimer.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

This invention relates to methods and apparatuses of decomposing chlorine substance and, more particularly, to methods and apparatuses for decomposing a substance such as chlorine by irradiating with rays.

[0002]

[Background Art]

Destruction of nature caused by the civilization, such as deforestation by acid rain, ozone layer destruction by chlorofluorocarbon and global warming caused by carbon dioxide gases has become problems, and thus environmental protection technologies are becoming required urgently these days.

[0003]

Particularly as waste disposal technologies, a plural number of decomposition technologies, such as decomposition of chlorofluorocarbon as a cause of ozone layer destruction, and decomposition of PCB (polychlorobiphenyl) which causes damage to living organisms after concentration and accumulation in the body of living organisms, are being developed these days.

[0004]

The structure of decomposition apparatus of chlorine substance us-

ing conventional chlorine substance treatment method is explained referring to various drawings. Fig. 10 is a cross-section view of a decomposition apparatus of chlorine substance using the conventional chlorine substance treatment method.

[0005]

A container for chemical reaction 102 is formed surrounding the periphery of a mercury-vapor lamp 101 which acts as an ultraviolet ray generator. The container for chemical reaction 102 is equipped with an inlet port 103 and an outlet port 104 of gases.

[0006]

As regards the decomposition apparatus of chlorine substance using such a chlorine substance treatment method, gas such as chlorofluorocarbon and oxygen is injected from the inlet port 103 into a reaction chamber 105 in the container for chemical reaction 102. Wherein, the mixed gas in the reaction chamber 105 is photodecomposed using ultraviolet rays generated by the mercury-vapor lamp 101. Chlorine gas and/or chlorine-based polymers are exhausted out of the container for chemical reaction 102 through the outlet port 104.

[0007]

[Subjects to be Solved by the Invention]

However, in such a conventional structure as described above, a mercury-vapor lamp is used as an ultraviolet ray generator with insufficient intensity of rays for decomposing chlorofluorocarbon, and accordingly there is a drawback that its decomposition capability for chlorofluorocarbon is low.

[0008]

Fig. 7 is a graph in which the relationship of a light absorption cross-section of various chlorofluorocarbon versus wavelength of light rays is

shown (Hubric, C. and Stuhl. F.: J. photochem, 12, P93 (1980)). As is shown in Fig. 7 there are various sorts of chlorofluorocarbon and the energy required to decompose chlorofluorocarbon increases as the number of chlorine elements decreases. Light absorption of chlorofluorocarbon except CCl_4 is small with light rays of wavelengths longer than 250 (nm). By the luminous wavelength of mercury-vapor lamp, 253.7 (nm), mainly used in chlorofluorocarbon decomposition, the light absorption cross-section is considerably small and thus decomposition is not sufficient. Further, by the luminous wavelength of mercury-vapor lamp, 185 (nm), the light absorption cross-section is large as is seen in Fig. 7. However, the output radiation density of light rays radiating from mercury-vapor lamp is several (mW/cm^2) and its radiation power of light is smaller than that of 253.7 (nm) light rays. Therefore its amount of photodecomposition becomes considerably small.

[0009]

Chlorofluorocarbon decomposition using light rays emitted from mercury-vapor lamp is low in decomposition capability as indicated above. An adoption of light rays of wavelength shorter than that of mercury-vapor lamp increases the decomposition capability and results in high decomposition efficiency.

[0010]

In the conventional photodecomposition of chlorofluorocarbon, oxygen gas is added with the purpose to enhance decomposition of chlorofluorocarbon. Photodecomposition of oxygen molecules produces oxygen atoms (oxygen radicals). By using the oxygen atoms (oxygen radicals) an effect of chlorine atom abstraction is produced. Therefore, producing a large number of oxygen atoms (oxygen radicals) promotes decomposition of chlorofluorocarbon.

[0011]

Fig. 8 is a graph indicating the relationship between absorption factor of oxygen molecules and wavelength of light rays (Refer to Ozonizer Handbook, P. 81 (1960) CORONA Publishing CO., LTD). As shown in Fig. 8, oxygen molecules can be decomposed in the light rays of 185 (nm) wavelength by the conventional mercury-vapor lamp but the absorption factor (light absorption cross-section) is remarkably small. Accordingly, decomposition capability for chlorofluorocarbon based on an effect of chlorine atom abstraction is small. With the limited decomposition capability, the time for decomposition of chlorofluorocarbon gets longer and thus high cost for the operation is incurred. Referring to Washida's Spectroscopic Research 40 (1991) P.235, in which there is a graph showing the relationship between light absorption cross-section of oxygen molecules and wavelength of light rays, characteristics of the light absorption cross-section of oxygen molecules is clearly described.

[0012]

The present invention has been made in light of the above-described problems. An object of the present invention concerns treatment methods of decomposing chlorine substance such as chlorofluorocarbon, providing treatment methods which have a high decomposition capability for chlorine substance and thus efficiently decompose chlorine substance.

[0013]

[Means in order to Solve the Subject]

To attain above mentioned object, treatment methods of chlorine substance in this invention are targeted around irradiation of chlorine substance in the oxygen mixed atmosphere with vacuum ultraviolet rays of 120

to 180 (nm) wavelength and thus decomposing chlorine substance.

[0014]

By setting fluorescence wavelength generated by an excimer lamp shorter than that of mercury-vapor lamp, that is, 180 (nm), a light absorption cross-section of chlorine substance increases. Decomposition of chlorine substance by fluorescent light from excimer is enhanced and thus decomposition efficiency is improved. Simultaneously, when oxygen molecules are irradiated with the fluorescent light of 120 to 180 (nm) wavelength from excimer, as indicated in Fig. 8, a large amount of oxygen radicals is generated. The volume of oxygen radicals is much larger than that of oxygen radicals by decomposition of oxygen molecules, which is generated by mercury-vapor lamp, because of difference between light absorption cross-section according to wavelength. Thereby chlorine substance is decomposed efficiently with higher effect of chlorine abstraction from chlorine substance induced by oxygen radicals.

[0015]

In order to improve decomposition efficiency for decomposition of chlorine substance and to simultaneously improve decomposition efficiency by means of chlorine abstraction effect by oxygen radicals, similar effect as described above can be achieved by using rare gases such as, most notably, xenon, argon and krypton.

[0016]

Further, treatment method of decomposition of chlorine substance in this invention involves processes in which, chlorine substance, in an oxygen mixed atmosphere, is irradiated with fluorescent light from xenon excimer, and the chlorine substance is decomposed.

[0017]

Wavelength of fluorescent light from xenon excimer resides in a range of about 150 to 195 (nm). By using fluorescent light from excimer whose wavelength is less than 180 (nm) at its upper limit in the above described range, a remarkably improved decomposition efficiency can be achieved with a large amount of fluorescent light from excimer to decompose chlorine substance and with its strong light intensity. Further, light of about 150 to 180 (nm) wavelength can efficiently generate oxygen radicals from oxygen molecules, which can provide an effect of chlorine abstraction that abstract chlorine atom from chlorine substance. The effect of chlorine atom abstraction by oxygen radicals can decompose chlorine substance efficiently.

[0018]

Still further, treatment apparatus of decomposition of chlorine substance in this involves: a container for intake of chlorine substance; maintaining oxygen atmosphere means for maintaining an oxygen mixed atmosphere in the container; and irradiation means for irradiating chlorine substance intake within the container with vacuum ultraviolet rays of 120 to 180 (nm) wavelength.

[0019]

Furthermore, treatment apparatus of decomposition of chlorine substance in this invention involves: a container for intake of chlorine substance; maintaining oxygen atmosphere means for maintaining an oxygen mixed atmosphere in the container; and irradiation means for irradiating chlorine substance intake within the container with fluorescent light from xenon excimer.

[0020]

[Embodiments of the Invention]

Hereinafter, the embodiments of the present invention will be explained with reference to the drawings. Fig. 1 (a) is a cross-section view of a first embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance. Fig. 1 (b) is a sectional view taken along the A – A' line and seen from the direction of the arrow in Fig. 1 (a).

[0021]

A discharge container 7 (container) having a decomposition process area 8 for decomposing chlorine substance is equipped with a meshed cylindrical electrode 3 (irradiation means) arranged around it in a coaxially cylindrical shape. Inside the discharge container 7, a cylindrical window tube 4 through which vacuum ultraviolet rays can pass is provided. Around the meshed cylindrical electrode 3, an insulating tube 2 which is made of quartz is arranged in a coaxially cylindrical shape. Around the insulating tube 2, a high voltage cylindrical electrode 1 (irradiation means) is arranged in a coaxially cylindrical shape. Between the insulating tube 2 and the high voltage cylindrical electrode 1, a surface 5 having a mirror finish is provided. In a discharge space 6 between the meshed cylindrical electrode 3 and the insulating tube 2, a gas such as xenon which has a fluorescence wavelength from excimer in the wavelength region of 120 to 180 (nm) is encapsulated. A power supply 9 is coupled to the meshed cylindrical electrode 3 and the high voltage cylindrical electrode 1. To the discharge container 7, maintaining oxygen atmosphere means, not shown, is attached.

[0022]

A photodecomposition apparatus 10 involves: a high voltage cylindrical electrode 1, an insulating tube 2, a meshed cylindrical electrode 3, a window tube 4, surface 5, a discharge space 6, a discharge container 7, a decomposition process area 8, a power supply 9, and maintaining oxygen

atmosphere means.

[0023]

Treatment method of chlorine substance utilizing photodecomposition apparatus 10 adopting aforementioned structure will be explained. First, oxygen is injected to the decomposition process area 8 from the outside of photodecomposition apparatus 10. Next, a gas of chlorofluorocarbon is immixed in the decomposition process area 8 under the oxygen mixed atmosphere. Then, a polarity alternating voltage is applied to the meshed cylindrical electrode 3 and the high voltage cylindrical electrode 1 from the power supply 9 which is coupled to them. Then, in the discharge space 6, dielectric barrier discharge occurs between the meshed cylindrical electrode 3 and the insulating tube 2. As a result, by means of the dielectric barrier discharge, vacuum ultraviolet rays (fluorescent light from xenon excimer) having a peak wavelength of 172 (nm) in its spectrum is generated from xenon. The generated vacuum ultraviolet rays pass through the meshed cylindrical electrode 3, and further pass through the window tube 4. With the passed-through vacuum ultraviolet rays, chlorofluorocarbon, oxygen and the like in decomposition process area 8 inside the discharge container 7 are irradiated.

[0024]

Under the circumstance described above, a chain of reactions indicated in formula (1) and in formula (2), thus performing photodecomposition of chlorine substance, take place subsequently.

Here, h: Planck's constant, 6.625×10^{-34} (J·s)

v: frequency

n: integer number

*: radical atom or radical molecule

[0025]

(formula 1)

$CCl_2F_2 + hv \rightarrow CClF_2^* + Cl^*$ ...(1)

[0026]

(formula 2)

$CClF_2^* + hv \rightarrow CF_2^* + Cl^*$ ...(2)

Amount of fluorescent light from xenon excimer, as is shown in Fig. 9, if its wavelength is 172 (nm) or less (hatched area A) where absorption factor of O_2 becomes higher, is as much as about 50% of the total amount of fluorescent light from xenon excimer (hatched area A + hatched area B). Therefore, the reaction shown in formula (3) takes place. Oxygen transforms into oxygen radical (O*) and the amount of oxygen radicals increases enormously.

[0027]

(formula 3)

$O_2 + hv \rightarrow 2O^*$ ... (3)

Further, a chain of reactions take place as shown in formula (4) and formula (5). Thus decomposition of chlorofluorocarbon is enhanced by the increase of effect of chlorine absorption by oxygen radicals.

[0028]

(formula 4)

$CCl_2F_2 + O^* \rightarrow CClF_2^* + ClO$ ...(4)

[0029]

(formula 5)

$CClF_2^* + O^* \rightarrow CF_2^* + ClO$ ...(5)

Furthermore, a chain of reactions by photodecomposition in formula (6), formula (7), and formula (8) take place as follows:

[0030]

(formula 6)

$CClF_2^* + Cl^* \rightarrow CF_2^* + Cl_2$ ...(6)

[0031]

(formula 7)

$ClO + O^* \rightarrow Cl^* + O_2$ ...(7)

[0032]

(formula 8)

$Cl^* + Cl^* \rightarrow Cl_2$ ...(8)

Through the chain of reactions of chlorofluorocarbons as above, the chlorofluorocarbon gases are decomposed into chlorine gas and/or chlorine-based polymers. Thus, at the final stage of the chain of reactions the chlorofluorocarbon gases are generally decomposed into chlorine and the like by the reaction as written in the formula (9).

[Brief Description of the Drawings]

[0033]

(formula 9)

$$nCCl_2F_2 \xrightarrow{hv} nCl_2 + \underset{F\ \ n}{C} \quad \ldots(9)$$

[0034]

The treatment method of chlorine substance by photodecomposition described above uses xenon as encapsulated gas in the discharge space 6. When the wavelength of the light generated by xenon by means of discharge (fluorescent light from xenon excimer) is compared with the 185 (nm) reso-

nance line of the conventional mercury-vapor lamp, the peak wavelength of xenon, 172 (nm), is shorter. The fluorescent light from xenon excimer having wavelength shorter than 180 (nm) dominates about 80% of the total amount of light from xenon excimer. Therefore, a light absorption cross-section by light from xenon excimer becomes larger than that by light from mercury-vapor lamp whose wavelength is 185 (nm).

[0035]

The power density of fluorescent light from xenon excimer of this invention is about 14 (mW/cm^2). It is larger than that of conventional mercury-vapor lamp. The emission intensity is also increased by about twice under the same power consumption. Thus, decomposition capability of chlorine substance, such as chlorofluorocarbon, is increased in a large amount based on the improvements in absorption factor and power density.

[0036]

Use of argon (peak wavelength of 126(nm)) and krypton (peak wavelength of 146.7(nm)) as encapsulated gas in discharge space 6 can generate a wavelength shorter than 180 (nm). Therefore, light absorption cross-section of argon and krypton are larger than that of mercury-vapor lamp, and the decomposition capabilities of chlorine substance by photodecomposition are improved.

[0037]

Further, by irradiating oxygen mixed with chlorofluorocarbon with fluorescent light of 172 (nm) from xenon excimer (or fluorescent light from argon excimer or fluorescent light from krypton excimer) which has shorter wavelength than 185 (nm) wavelength of mercury-vapor lamp, light absorption factor of oxygen molecules rapidly increases by more than an order of magnitude and thus oxygen molecules are decomposed and transformed into

oxygen radicals. When a large number of oxygen radicals exist, effect of chlorine abstraction from chlorine substance increases and decomposition of chlorofluorocarbon is promoted.

[0038]

The vacuum ultraviolet ray is generated in the process of dielectric barrier discharge from the insulating tube 2 and the meshed cylindrical electrode 3 with many openings. Because the outer surface of insulating tube 2 is made of transparent material, the ray is reflected from the mirror finished surface 5. Then, the light intensity to decompose chlorine substance such as chlorofluorocarbon is further increased, and improvement in chlorofluorocarbon decomposition capability is attained.

[0039]

A cylinder structure made of quartz surrounding the meshed cylindrical electrode 3 can also be used. The structure described above has preferable effect that metal sputtering by discharge does not take place. Herein, the structure of meshed cylindrical electrode 3 can be a wired mesh (a state of wrapping wires around the discharge container 7). By adopting this construction a cost down can be achieved.

[0040]

Next, a second embodiment of the decomposition apparatus of chlorine substance using a treatment method of chlorine substance will be explained with reference to the drawings. Here, for each embodiment below the same numerals and codes are used for the same components in the first embodiment and duplicated explanation is omitted.

[0041]

Features of the second embodiment reside in its structure where a plural number of photodecomposition apparatuses 10 of the first embodi-

ment are arranged in parallel in equal distance from each other, and water channels through which cooling water is able to circulate around each photodecomposition apparatus 10 are provided.

[0042]

Fig. 2 (a) is a cross-section view of the second embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance. Fig. 2 (b) is a sectional view taken along the A – A' line and seen from the direction of the arrow in Fig. 2 (a).

[0043]

In Fig. 2 (a), solid line arrows indicate flow of chlorine substance such as chlorofluorocarbon and broken line arrows indicate flow of cooling water respectively and schematically. As shown in Fig. 2, for example 21 units of photodecomposition apparatuses 10 are arranged in a cylindrically shaped container in equal distance from and without touching each other in a criss-cross pattern. In the space between one photodecomposition apparatus 10 and adjacent photodecomposition apparatus 10, channels are laid out through which cooling water is able to circulate. A photodecomposition apparatus 11 is constructed with an arrangement of plural number of photodecomposition apparatuses 10.

[0044]

A treatment method of chlorine substance using photodecomposition apparatus 10 adopting aforementioned structure will be explained. First, oxygen is injected to the decomposition process area 8 from the outside of photodecomposition apparatus 10. Next, a gas of chlorofluorocarbon is immixed in the decomposition process area 8 under the oxygen mixed atmosphere. Then, a polarity alternating voltage is applied to the meshed cylindrical electrode 3 and the high voltage cylindrical electrode 1 from the

power supply which is coupled to them. Then, in the discharge space 6 between the meshed cylindrical electrode 3 and the insulating tube 2, dielectric barrier discharge occurs. As a result, by means of dielectric barrier discharge, vacuum ultraviolet rays (fluorescent light from xenon excimer) having a peak wavelength of 172 (nm) in its spectrum is generated from xenon. The generated vacuum ultraviolet rays pass through the meshed cylindrical electrode 3, and further pass through the window tube 4. With the passed-through vacuum ultraviolet rays, chlorofluorocarbon, oxygen and the like in decomposition process area 8 inside the discharge container are irradiated.

[0045]

The amount of fluorescent light from xenon excimer, as is shown in Fig. 9, if its wavelength is 172 (nm) or below (hatched area A), is about as much as 50% of the total amount of fluorescent light from xenon excimer (hatched area A + hatched area B). Oxygen transforms into oxygen radical (O*) and the amount of oxygen radicals increases enormously. With the increase of oxygen radicals, effect of chlorine abstraction by oxygen radicals increases and decomposition of chlorofluorocarbon is promoted.

[0046]

As is indicated above, the chlorofluorocarbon gas is decomposed and disposed of as chlorine gas and/or chlorine-based polymers. The treatment method of chlorine substance by photodecomposition described above uses xenon as encapsulated gas in the discharge space. When the wavelength of the light generated by xenon by means of discharge (fluorescent light from xenon excimer) is compared with the 185 (nm) resonance line of the conventional mercury-vapor lamp, the peak wavelength of xenon, 172 (nm), is shorter. The fluorescent light from xenon excimer of wavelength shorter

than 180 (nm) dominates about 80% of the total amount of fluorescent light from xenon excimer. Then, a light absorption cross-section by light from xenon excimer becomes larger than that by light from mercury-vapor lamp whose wavelength is 185 (nm).

[0047]

The power density of fluorescent light from xenon excimer of this invention is about 14 (mW/cm^2). It is larger than that of conventional mercury-vapor lamp. The emission intensity is also increased by about twice under the same power consumption. Thus, decomposition capability of chlorine substance, such as chlorofluorocarbon, is increased in a large amount based on the improvements in absorption factor and power density.

[0048]

Use of argon (peak wavelength of 126(nm)) and krypton (peak wavelength of 146.7(nm)) as encapsulated gas in the discharge space can generate a wavelength shorter than 180 (nm). Therefore, light absorption cross-section of argon and krypton are larger than that of mercury-vapor lamp, and the decomposition capabilities of chlorine substance by photodecomposition are improved.

[0049]

Further, by irradiating oxygen mixed with chlorofluorocarbon with fluorescent light of 172 (nm) from xenon excimer (or fluorescent light from argon excimer or fluorescent light from krypton excimer) which has shorter wavelength than 185 (nm) wavelength of mercury-vapor lamp, light absorption factor of oxygen molecules rapidly increases by more than an order of magnitude and thus oxygen molecules are decomposed and transformed into oxygen radicals. When a large number of oxygen radicals exist, effect of chlorine abstraction from chlorine substance increases and decomposition of

chlorofluorocarbon is promoted.

[0050]

The vacuum ultraviolet ray is generated in the process of dielectric barrier discharge from the insulating tube 2 and the meshed cylindrical electrode 3 with many openings. Because the outer surface of insulating tube 2 is made of transparent material, the ray is reflected from the mirror finished surface 5. Then, the light intensity to decompose chlorine substance such as chlorofluorocarbon is further increased, and improvement in chlorofluorocarbon decomposition capability is attained.

[0051]

Further, cooling water circulates through the spaces between photodecomposition apparatuses 10, thus removing heat generated from photodecomposition apparatuses 10. The photodecomposition apparatus 11 described above, which uses plural number of photodecomposition apparatuses 10 as are shown in Fig. 2, can decompose a large amount of chlorine substance, such as chlorofluorocarbon gas, efficiently in a short period of time.

[0052]

Next, a third embodiment of the decomposition apparatus of chlorine substance using a treatment method of chlorine substance will be explained with reference to the drawings. Features of the third embodiment reside in a structure where there is a cylindrically shaped metal in the decomposition space.

[0053]

Fig. 3 (a) is a cross-section view of the third embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance. Fig. 3 (b) is a sectional view taken along the A – A' line and seen from the direction of the arrow in Fig. 3 (a).

[0054]

A discharge container 7 having a decomposition process area 8 is equipped with a meshed cylindrical electrode 3 around it in a coaxially cylindrical shape. Inside the discharge container 7, a cylindrical window tube 4 through which vacuum ultraviolet rays can pass is provided. Around the meshed cylindrical electrode 3, an insulating tube 2 which is made of quartz is arranged in a coaxially cylindrical shape. Around the insulating tube 2, a high voltage cylindrical electrode 1 is arranged in a coaxially cylindrical shape. Between the insulating tube 2 and the high voltage cylindrical electrode 1, a surface 5 having a mirror finish is provided. In a discharge space 6 between the meshed cylindrical electrode 3 and the insulating tube 2, a gas, such as xenon, which has radiates fluorescent light having wavelength region of 120 to 180 (nm) from its excimer, is encapsulated. A power supply 9 is coupled to the meshed cylindrical electrode 3 and the high voltage cylindrical electrode 1. Inside the decomposition process area 8, a cylindrically shaped metal pipe 40 is inserted.

[0055]

As described above, a photodecomposition apparatus 11 is composed of a high voltage cylindrical electrode 1, an insulating tube 2, a meshed cylindrical electrode 3, a window tube 4, a surface 5, a discharge space 6, a discharge container 7, a decomposition process area 8, a power supply 9, and a metal pipe 40.

[0056]

Treatment method of chlorine substance using photodecomposition apparatus 11 adopting aforementioned structure will be explained. Oxygen is injected to the decomposition process area 8 from the outside of photodecomposition apparatus 11. A gas of chlorofluorocarbon is immixed in the

decomposition process area 8 under the oxygen mixed atmosphere. A polarity alternating voltage is applied to the meshed cylindrical electrode 3 and the high voltage cylindrical electrode 1 from the power supply 9 which is coupled to them. Then, in the discharge space 6 between the meshed cylindrical electrode 3 and the insulating tube 2 dielectric barrier discharge occurs. As a result, by means of the dielectric barrier discharge, vacuum ultraviolet rays having a peak wavelength of 172 (nm) in its spectrum (fluorescent light from xenon excimer) is generated from xenon. The generated vacuum ultraviolet rays pass through the meshed cylindrical electrode 3, and further pass through the window tube 4. With the passed-through vacuum ultraviolet rays, chlorofluorocarbon, oxygen and the like in decomposition process area 8 inside the discharge container are irradiated. Consequently, photodecomposition will be performed.

[0057]

As shown in Fig. 9, the amount of light having wavelength of 172 (nm) or less (hatched area A) in the fluorescent light from xenon excimer, is about as much as 50% of the total amount of fluorescent light from xenon excimer (hatched area A + hatched area B). Oxygen transforms into oxygen radical and the amount of oxygen radicals increases enormously.

[0058]

The oxygen radicals abstract chlorine in chlorofluorocarbon gas by the effect of chlorine abstraction and decomposition of chlorofluorocarbon is further promoted. By the photodecomposition reaction of chlorofluorocarbon as mentioned above, chlorofluorocarbon gases are eventually decomposed into chlorine gas and/or chlorine-based polymers.

[0059]

The treatment method of chlorine substance by photodecomposition

described above uses xenon as encapsulated gas in the discharge space 6. When the wavelength of the light generated by xenon by means of discharge (fluorescent light from xenon excimer) is compared with the 185 (nm) resonance line of the conventional mercury-vapor lamp, the peak wavelength of xenon, 172 (nm), is shorter. The fluorescent light from xenon excimer of wavelength shorter than 180 (nm) dominates about 80% of the total amount of fluorescent light from xenon excimer. Then, a light absorption cross-section by light from xenon becomes larger than that by light having wavelength of mercury-vapor lamp.

[0060]

The power density of fluorescent light from xenon excimer of this invention is about 14 (mW/cm^2). It is larger than that of conventional mercury-vapor lamp. The emission intensity is also increased by about twice under the same power consumption. Thus, decomposition capability of chlorine substance, such as chlorofluorocarbon, is increased in a large amount based on the improvements in absorption factor and power density.

[0061]

Use of argon (peak wavelength of 126(nm)) and krypton (peak wavelength of 146.7(nm)) as encapsulated gas in discharge space 6 can generate a wavelength shorter than 180 (nm). Therefore, light absorption cross-section of argon and krypton becomes larger than a light absorption cross-section of mercury-vapor lamp, and the decomposition capabilities of chlorine substance by photodecomposition are improved.

[0062]

Further, by irradiating oxygen mixed with chlorofluorocarbon with fluorescent light of 172 (nm) from xenon excimer (or fluorescent light from argon excimer or krypton excimer) which has shorter wavelength than 185

(nm) wavelength of mercury-vapor lamp, light absorption factor of oxygen molecules rapidly increases by more than an order of magnitude and thus oxygen molecules are decomposed and transformed into oxygen radicals. When a large number of oxygen radicals exist, effect of chlorine abstraction from chlorine substance increases and decomposition of chlorofluorocarbon is promoted.

[0063]

The vacuum ultraviolet ray is generated in the process of dielectric barrier discharge from the insulating tube 2 and the meshed cylindrical electrode 3 with many openings. Because the outer surface of insulating tube 2 is made of transparent material, the ray is reflected from the mirror finished surface 5. Then, the light intensity to decompose chlorine substance such as chlorofluorocarbon is further increased, and improvement in chlorofluorocarbon decomposition capability is attained.

[0064]

The chlorofluorocarbon gas in decomposition process area 8 is irradiated with the vacuum ultraviolet rays with uniform intensity from around the decomposition process area 8. Therefore, by providing the metal pipe 40, decomposition of chlorofluorocarbon gas both in the front surface and the center of discharge container 7 by means of vacuum ultraviolet rays irradiation becomes performed evenly and thus the decomposition efficiency of chlorofluorocarbon is improved.

[0065]

The metal pipe 40 in which coolant, such as water or the like, circulate in its hollow center, can also cool down the photodecomposition apparatus 11. It has a cooling effect of photodecomposition apparatus 11. Next, a fourth embodiment of the decomposition apparatus of chlorine substance

using a treatment method of chlorine substance will be explained with reference to the drawings.

[0066]

Feature of the fourth embodiment is that a decomposition process area is located outside of discharge space. Fig. 4 (a) is a cross-section view of the fourth embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance. Fig. 4 (b) is a sectional view taken along the A – A' line and seen from the direction of the arrow in Fig. 4 (a).

[0067]

Around a high voltage cylindrical electrode 51, a surface 52 which has a mirror finish enabling reflection of an incoming light is formed in a coaxially cylindrical shape. Further around it, an insulating tube 53 made of quartz is arranged in a coaxially cylindrical shape with the surface 52. Still further around it, a meshed cylindrical electrode 55 is arranged in a coaxially cylindrical shape with an insulating tube 53. Between the insulating tube 53 and the meshed cylindrical electrode 55, a discharge space 54 is provided in which a gas, such as xenon radiates fluorescent light having wavelength region of 120 to 180 nm from its excimer. A power supply 56 is coupled to the meshed cylindrical electrode 55 and the high voltage cylindrical electrode 51. Around the meshed cylindrical electrode 55, a cylindrically shaped window tube 57 through which vacuum ultraviolet rays can pass is arranged in a coaxially cylindrical shape with the meshed cylindrical electrode 55. Around the window tube 57, an outer wall 59 is arranged in a coaxially cylindrical shape with the window tube 57. Between the window tube 57 and the outer wall 59, a decomposition process area 58 is arranged.

[0068]

A photodecomposition apparatus 50 is composed of a high voltage cylindrical electrode 51, a surface 52, an insulating tube 53, a discharge space 54, a meshed cylindrical electrode 55, a power supply 56, a window tube 57, a decomposition process area 58, and outer wall 59 as described above.

[0069]

Treatment method of chlorine substance by photodecomposition apparatus 50 adopting aforementioned structure will be explained. Oxygen is injected to the decomposition process area 58 from the outside of photodecomposition apparatus 50. A gas of chlorofluorocarbon is immixed in the decomposition process area 58 under the oxygen mixed atmosphere. A polarity alternating voltage or pulse voltage is applied to the meshed cylindrical electrode 55 and the high voltage cylindrical electrode 51 from the power supply 56 which is coupled to them. Then, in the discharge space 54 between the meshed cylindrical electrode 55 and the insulating tube 53 dielectric barrier discharge occurs. As a result, by means of the dielectric barrier discharge, vacuum ultraviolet rays (fluorescent light from xenon excimer) having a peak wavelength of 172 (nm) in its spectrum is generated from xenon. The generated vacuum ultraviolet rays pass through the meshed cylindrical electrode 55, and further pass through the window tube 57. With the passed-through vacuum ultraviolet rays, chlorofluorocarbon, oxygen and the like in decomposition process area 58 inside the outer wall 59 are irradiated. Consequently, photodecomposition will be performed.

[0070]

As is shown in Fig. 9, the amount of light having wavelength of 172 (nm) or less in the fluorescent light from xenon excimer (hatched area A) is about as much as 50% of the total amount of fluorescent light from xenon

excimer (hatched area A + hatched area B). Thus, oxygen transforms into oxygen radical and the amount of oxygen radicals increases enormously.

[0071]

The oxygen radicals abstract chlorine in chlorofluorocarbon gas by the effect of chlorine abstraction and promote the decomposition of chlorofluorocarbon. By the photodecomposition reaction of chlorofluorocarbons as mentioned above, chlorofluorocarbon gases are eventually decomposed into chlorine gas and/or chlorine-based polymers.

[0072]

The treatment method of chlorine substance by photodecomposition described above uses xenon as encapsulated gas in the discharge space 54. When the wavelength of the light generated by xenon by means of discharge (fluorescent light from xenon excimer) is compared with the 185 (nm) resonance line of the conventional mercury-vapor lamp, the peak wavelength of xenon, 172 (nm), is shorter. The fluorescent light from xenon excimer of wavelength shorter than 180 (nm) dominates about 80% of the total amount of fluorescent light from xenon excimer. Then, a light absorption cross-section by light from xenon becomes larger than a light absorption cross-section by light having wavelength of mercury-vapor lamp.

[0073]

The power density of fluorescent light from xenon excimer of this invention is about 14 (mW/cm^2). It is larger than that of conventional mercury-vapor lamp. The emission intensity is also increased by about twice under the same power consumption. Thus, decomposition capability of chlorine substance, such as chlorofluorocarbon, is increased in a large amount based on the improvements in absorption factor and power density.

[0074]

Use of argon (peak wavelength of 126(nm)) and krypton (peak wavelength of 146.7(nm)) as encapsulated gas in discharge space 54 can generate a wavelength shorter than 185 (nm). Therefore, light absorption cross-section of argon and krypton are larger than that of mercury-vapor lamp, and the decomposition capabilities of chlorine substance by photodecomposition are improved.

Further, by irradiating oxygen mixed with chlorofluorocarbon with fluorescent light of 172 (nm) from xenon excimer (or fluorescent light from argon excimer or fluorescent light from krypton excimer) which has shorter wavelength than 185 (nm) wavelength of mercury-vapor lamp, light absorption factor of oxygen molecules rapidly increases by more than an order of magnitude and thus oxygen molecules are decomposed and transformed into oxygen radicals. When a large number of oxygen radicals exist, effect of chlorine abstraction from chlorine substance increases and decomposition of chlorofluorocarbon is promoted.

[0075]

The vacuum ultraviolet ray is generated in the process of dielectric barrier discharge from the insulating tube 53 and the meshed cylindrical electrode 55 with many openings. Because the outer surface of insulating tube 53 is made of transparent material, the ray is reflected from the mirror finished surface 52. Then, the light intensity to decompose chlorine substance such as chlorofluorocarbon is further increased, and improvement in chlorofluorocarbon decomposition capability is attained.

[0076]

The decomposition process area 58 is provided in the outside of the discharge space 54. Chlorofluorocarbon gases residing inside of it are evenly irradiated with vacuum ultraviolet rays from around the

chlorofluorocarbon gases. Thus, decomposition of chlorofluorocarbon gases is evenly performed and decomposition efficiency of chlorofluorocarbon is improved.

[0077]

The structure of the high voltage cylindrical electrode 51 can be a cylindrical shape with a hollow in the center. It is possible to allow coolant such as water to circulate through the hollow to cool down the photodecomposition apparatus 50. Next, a fifth embodiment of the decomposition apparatus of chlorine substance using a treatment method of chlorine substance will be explained with reference to the drawings.

[0078]

Feature of the fifth embodiment resides in a form of electrode which is shaped in a flat plate. Fig. 5 (a) is a cross-section view of the fifth embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance. Fig. 5 (b) is an enlarged view of the meshed electrode in the decomposition apparatus of chlorine substance using a treatment method of chlorine substance according to the fifth embodiment.

[0079]

Around an electrode plate 21, an insulator 22 made of quartz is provided. The surface of insulator 22 has a mirror finish in order to reflect light sufficiently. A high voltage electrode 30 is constructed from the electrode plate 21 and the insulator 22. In an arbitrary distance from the high voltage electrode 30, a meshed electrode 24 is arranged in parallel relation to it. In an arbitrary distance apart with the meshed electrode 24, a window plate 26 made of quartz is arranged. In an arbitrary distance from the window plate 26, another window plate 26 made of quartz is positioned to

face each other. In between the window plates 26, a decomposition process area 27 in which chlorine substance such as chlorofluorocarbon is encapsulated is arranged. In an arbitrary distance from the window plate 26, a meshed electrode 24 is arranged. In an arbitrary distance from the meshed electrode 24, a high voltage electrode 30 is arranged. Additionally, on the surfaces of each meshed electrode 24 on the side facing adjacent discharge spaces 23, boards made of quartz may be fitted.

[0080]

Using aforementioned structures arranged symmetrically, where the high voltage electrode 30 forms a central axis of symmetry, a decomposition apparatus 31 is constructed. The high voltage electrode 30, window plates 26 and meshed electrodes 24 are arranged by being held on supports 28. Each meshed electrode 24 is grounded, each high voltage electrode 30 is electrically connected, and a power supply 29 coupled to them. Between high voltage electrode 30 and meshed electrode 24 is the discharge space 23. In the discharge space 23, a gas such as xenon which radiates fluorescent light having wavelength region of 120 to 180 (nm) from its excimer is encapsulated.

[0081]

Fig. 5 (b) illustrates the structure of the meshed electrode 24 and the supports 28 and arrows show the flow direction of xenon. The photodecomposition apparatus 31 is constructed from high voltage electrodes 30 (electrode plates 21 and insulators 22), discharge spaces 23, meshed electrodes 24, window plates 26, supports 28, and a power supply 31.

[0082]

Treatment method of chlorine substance by photodecomposition apparatus 31 adopting aforementioned structure will be explained. High

voltage of alternating polarity is applied to the high voltage electrode 30 and the meshed electrode 24. Dielectric barrier discharge occurs in the discharge space 23 and xenon encapsulated in the discharge space 23 generates fluorescent light from its excimer. Fluorescent light from xenon excimer radiates through window plates 26 on both sides of the decomposition area 27 and chlorofluorocarbon gas is decomposed.

[0083]

The treatment method of chlorine substance by photodecomposition described above uses xenon as encapsulated gas in the discharge space 23. When the wavelength of the light generated by xenon by means of discharge (fluorescent light from xenon excimer) is compared with the 185 (nm) resonance line of the conventional mercury-vapor lamp, the peak wavelength of xenon, 172 (nm), is shorter. The fluorescent light from xenon excimer of wavelength shorter than 180 (nm) dominates about 80% of the total amount of fluorescent light from xenon excimer. Therefore, a light absorption cross-section of xenon excimer is larger than a light absorption cross-section by light having wavelength of mercury-vapor lamp.

[0084]

The power density of fluorescent light from xenon excimer of this invention is about 14 (mW/cm^2). It is larger than that of conventional mercury-vapor lamp. The emission intensity is also increased by about twice under the same power consumption. Thus, decomposition capability of chlorine substance, such as chlorofluorocarbon, is increased in a large amount based on the improvements in absorption factor and power density.

[0085]

Use of argon (peak wavelength of 126(nm)) and krypton (peak wavelength of 146.7(nm)) as encapsulated gas in discharge space 23 can generate

a wavelength shorter than 185 (nm). Therefore, light absorption cross-section of argon and krypton become larger than that of mercury-vapor lamp, and the decomposition capabilities of chlorine substance by photodecomposition are improved.

[0086]

Further, by irradiating oxygen mixed with chlorofluorocarbon with fluorescent light of 172 (nm) from xenon excimer (or fluorescent light from argon excimer or fluorescent light from krypton excimer) which has shorter wavelength than 185 (nm) wavelength of mercury-vapor lamp, light absorption factor of oxygen molecules rapidly increases by more than an order of magnitude and thus oxygen molecules are decomposed and transformed into oxygen radicals. When a large number of oxygen radicals exist, effect of chlorine abstraction from chlorine substance increases and decomposition of chlorofluorocarbon is promoted.

[0087]

The vacuum ultraviolet ray is generated in the process of dielectric barrier discharge from the insulator 22 and the meshed cylindrical electrode 30 with many openings. Because the window plates 26 are made of transparent material, the ray is reflected from the electrode plates 21 with mirror finished surface 21. Then, the light intensity to decompose chlorine substance such as chlorofluorocarbon is further increased, and improvement in chlorofluorocarbon decomposition capability is attained.

[0088]

Furthermore, because shape of the electrode is a flat plane, illuminance distribution by fluorescent light from excimer for irradiating chlorofluorocarbon is even and an efficient photodecomposition of chlorofluorocarbon can be expected. Next, a sixth embodiment of the de-

composition apparatus of chlorine substance using a treatment method of chlorine substance will be explained with reference to the drawings.

[0089]

The same numerals and codes are used for the same components in the fifth embodiment, and duplicated explanation is omitted. Feature of the sixth embodiment resides in a structure in which a plural number of photodecomposition apparatuses 31 are arranged in horizontal and vertical directions, and between the photodecomposition apparatuses 31 arranged in vertical direction cooling channels are formed.

[0090]

Fig. 6 (a) is a cross-section view of the sixth embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance. Fig. 6 (b) is a sectional view taken along the A – A' line and seen from the direction of the arrow in Fig. 6 (a). The solid line arrows in Fig. 6 (a) indicate flow of toxic chlorine substance such as chlorofluorocarbon and broken line arrows indicate flow of cooling water respectively and schematically.

[0091]

For example, four rows of photodecomposition apparatuses 31 are arranged, for example, in a container in the shape of a rectangular solid. In between a photodecomposition apparatus 31 and another photodecomposition apparatus 31 adjacent in the vertical direction, a channel 41 through which coolant such as water is able to circulate is provided.

[0092]

A photodecomposition apparatus 42 is constructed from a plural number of photodecomposition apparatuses 31 and channels 41. The treatment method of chlorine substance by photodecomposition described

above is using xenon as encapsulated gas in the discharge space of the photodecomposition apparatus 31. When the wavelength of the light generated by xenon by means of discharge (fluorescent light from xenon excimer) is compared with the 185 (nm) resonance line of the conventional mercury-vapor lamp, the peak wavelength of xenon, 172 (nm), is shorter. The fluorescent light from xenon excimer of wavelength shorter than 180 (nm) dominates about 80% of the total amount of fluorescent light from xenon excimer. Then, a light absorption cross-section by light from xenon becomes larger than a light absorption cross-section by light having wavelength of mercury-vapor lamp.

[0093]

The power density of fluorescent light from xenon excimer of this invention is about 14 (mW/cm^2). It is larger than that of conventional mercury-vapor lamp. The emission intensity is also increased by about twice under the same power consumption. Thus, decomposition capability of chlorine substance, such as chlorofluorocarbon, is increased in a large amount based on the improvements in absorption factor and power density.

[0094]

Use of argon (peak wavelength of 126(nm)) and krypton (peak wavelength of 146.7(nm)) as encapsulated gas in discharge space can generate a wavelength shorter than 185 (nm). Therefore, light absorption cross-section of argon and krypton become larger than that of mercury-vapor lamp, and the decomposition capabilities of chlorine substance by photodecomposition are improved.

Further, by irradiating oxygen mixed with chlorofluorocarbon with fluorescent light of 172 (nm) from xenon excimer (or fluorescent light from argon excimer or fluorescent light from krypton excimer) which has shorter

wavelength than 185 (nm) wavelength of mercury-vapor lamp, light absorption factor of oxygen molecules rapidly increases by more than an order of magnitude and thus oxygen molecules are decomposed and transformed into oxygen radicals. When a large number of oxygen radicals exist, effect of chlorine abstraction from chlorine substance increases and decomposition of chlorofluorocarbon is promoted.

[0095]

Further, because shape of the electrode is a flat plane, illuminance distribution by excimer fluorescence for irradiating chlorofluorocarbon is even and an efficient photodecomposition of chlorofluorocarbon can be expected. Furthermore, cooling water curculates through the channels 41 among the photodecomposition apparatuses 31, thus absorbing heat originated in photodecomposition apparatuses 31 and cooling them down.

[0096]

Using photodecomposition apparatus 42 whose function is explained above, a large amount of chlorine substance such as chlorofluorocarbon is decomposed in a short period of time efficiently. The present invention is not intended to be limited to the above-described embodiments, and various changes may be made therein without departing from the spirit of the present invention. For example, around the meshed cylindrical electrode insulator can be coated. Photodecomposition apparatus using a treatment method of chlorine substance is not limited in its construction such as placement and number of units and figuration of photodecomposition apparatuses constructing the apparatus regardless of the presence or absence of coolant such as cooling water, at least when it can decompose chlorine substance properly. Additionally, metal pipes should at least reduce the capacity of the decomposition process area. In addition, metal pipes can be made

of glass and any figuration, number of units, and material used can be accepted. As for materials for the window in order to use excimer fluorescence of much shorter wavelengths (vacuum ultraviolet ray) compared with the transmission wavelength of quartz, magnesium fluoride and calcium fluoride and the like can be adopted. Although chlorofluorocarbons are taken as an example of putting the treatment method of chlorine substance to use, trichloroethylene which also includes chlorine can similarly be encapsulated and photodecomposed in the decomposition process area under oxygen mixed atmosphere.

[0097]

[Effect of the Invention]

With the configuration described above, the present invention allows elimination of or detoxification by decomposition of chlorine substance such as chlorofluorocarbons to be achieved stably and effectively with high elimination ratio and decomposition rate.

[Brief Description of Drawings]

Fig. 1 is a cross-section view of a first embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance according to the present invention.

Fig. 2 is a cross-section view of a second embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance according to the present invention.

Fig. 3 is a cross-section view of a third embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance according to the present invention.

Fig. 4 is a cross-section view of a fourth embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine sub-

stance according to the present invention.

Fig. 5 is a cross-section view of a fifth embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance according to the present invention.

Fig. 6 is a cross-section view of a sixth embodiment of decomposition apparatus of chlorine substance using a treatment method of chlorine substance according to the present invention.

Fig. 7 is a graph indicating a relationship between light absorption cross-section of various chlorofluorocarbon versus wavelength of light rays.

Fig. 8 is a graph indicating a relationship of absorption factor of oxygen molecule versus wavelength of light rays.

Fig. 9 is a graph indicating a relationship of emission spectrum from excimer versus wavelength of each rare gas.

Fig. 10 is a cross-section view of the decomposition apparatus of chlorine substance using conventional treatment method of chlorine substance.

[Explanation of Reference Numerals]

1, 51	high voltage cylindrical electrode
2, 53	insulating tube
3, 55	meshed cylindrical electrode
4, 57	window tube
5, 52	surface
6, 23, 54	discharge space
7	discharge container
8, 27, 58	decomposition process area
9, 29, 56	power supply
10, 11, 31, 42, 50	photodecomposition apparatus

21	electrode plate
22	insulator
24	meshed electrode
26	window plate
28	supports
30	high voltage electrode
40	metal pipe
41	channel
59	outer wall

Fig.10

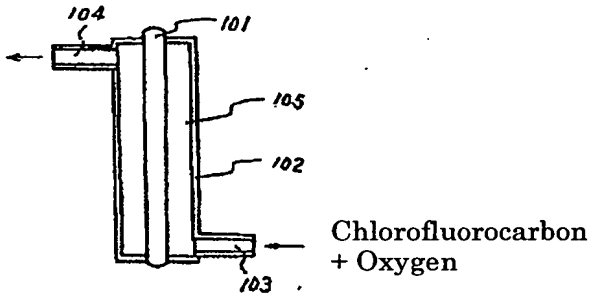


Fig.1

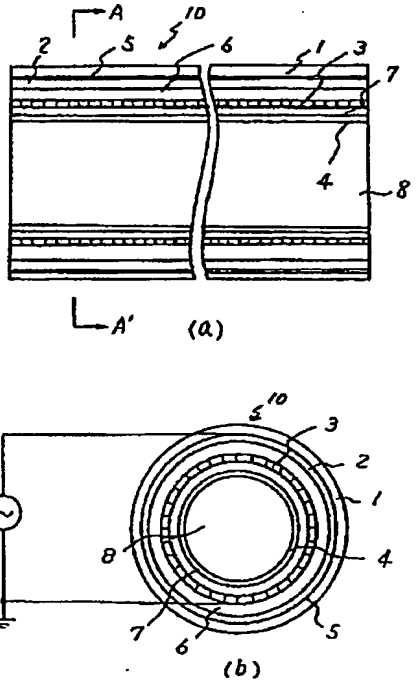


Fig.2

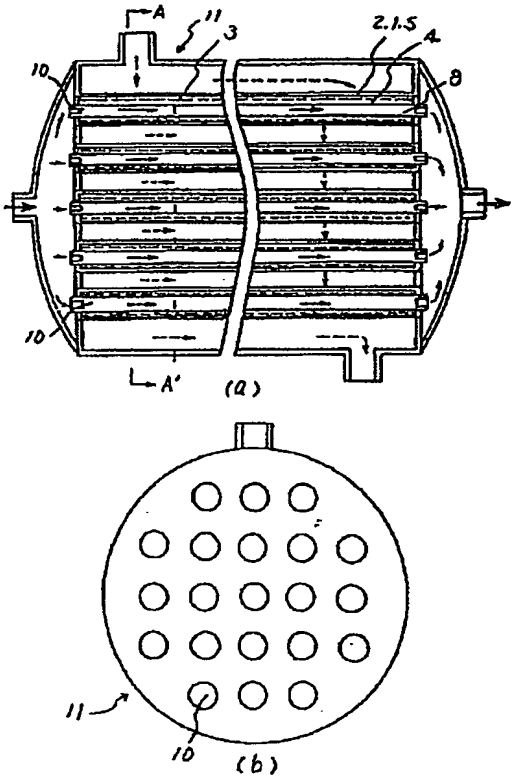


Fig.3

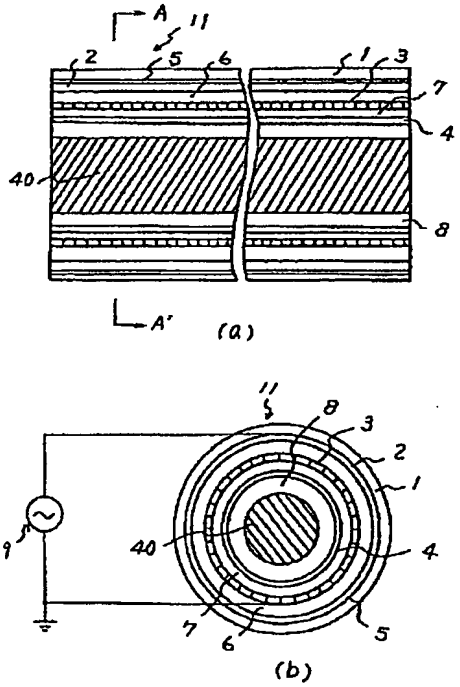


Fig.7

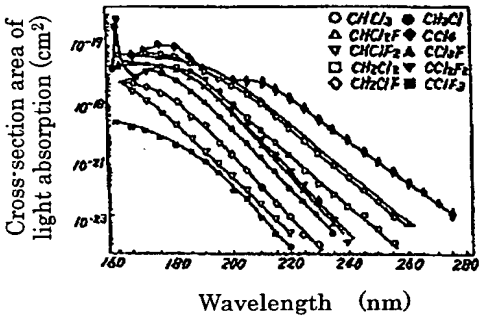
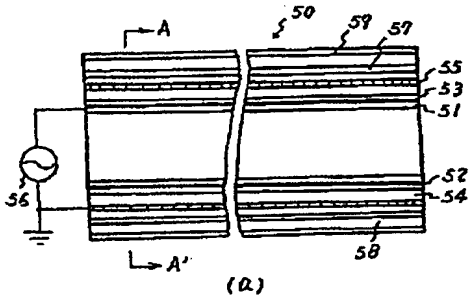


Fig.4



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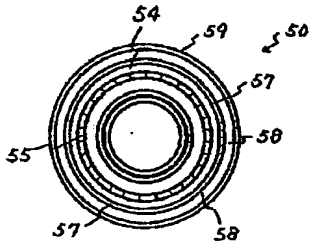
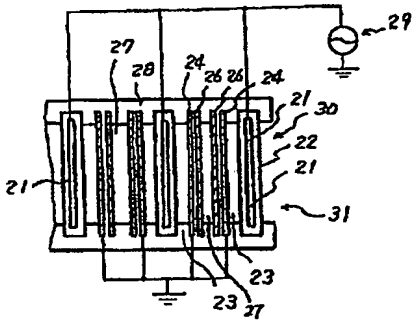


(b)

Fig.5



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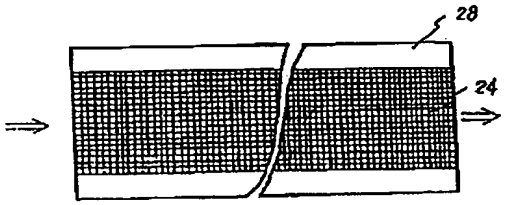
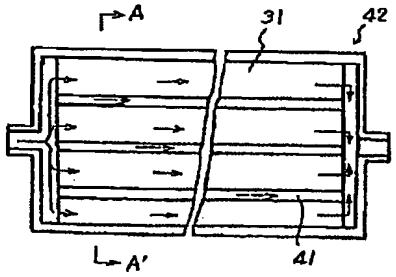


(b)

Fig.6



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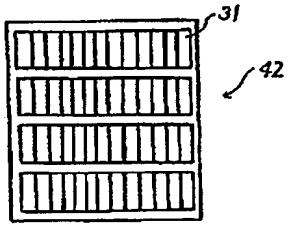


(b)

Fig.8

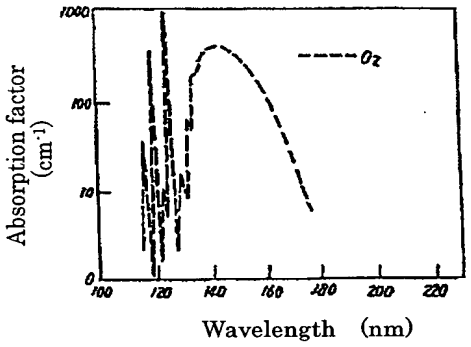
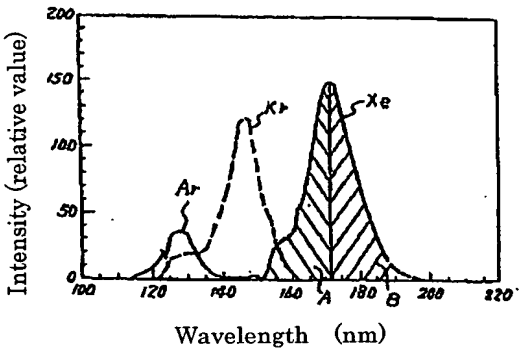


Fig.9


Intensity (relative value)
200
150
100
50
0
Ar
Kr
Xe
100
120
140
160
A
180
B
200
220
Wavelength (nm)